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Influence of Kinetic Coupling in Rectilinear Coordinates on the Vibrational Spectrum of Fluoroform

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Abstract

The vibrational energy levels of Fluoroform have been computed with and without the kinetic coupling terms of the Eckart-Watson Hamiltonian by using the vibrational mean field configuration interaction method. The results are well-converged as demonstrated by a comparison with those obtained with other variational methods when kinetic coupling is omitted. It is found that kinetic coupling is not negligible for this system. The wave number difference with and without kinetic coupling is 37 cm^{-1} for the ν_1 (CH-stretching) fundamental transition and can be larger than 60 cm^{-1} in the ν_1 - ν_4 (HCF bending) overtones.

Key words: vibrational mean field configuration interaction, kinetic coupling operator, Fermi resonance.

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1 Introduction

The quantum dynamics of the CH overtones of fluoroform CF_3H has been studied experimentally [1] as well as theoretically [2–4] in order to characterize the intramolecular vibrational-energy redistribution (IVR) that follows excitation of the CH stretching mode. The vibrational degrees-of-freedom of the system can be partitioned into, on one hand, the CH stretching mode (ν_1 -mode in spectroscopic notation) and the doubly degenerate FCH bending mode (ν_4 -mode) which constitute the “chromophore” of the molecule, since the bright states correspond to excitation to these modes, and, on the other hand, the rest of the modes that constitutes the “bath” in which the chromophore is immersed. The theoretical description of the system is complicated because strong Fermi resonances couple states within the chromophore and because a network of anharmonic interactions connect the chromophore bright states with dark states of the bath. Moreover the presence of a light atom suggests that kinetic coupling is far from being negligible. So, describing the vibrational energy level pattern of such a system is quite challenging.

A correct understanding of the spectroscopy, dynamics and reactivity of such a molecule requires an accurate representation of the molecular quantum eigenstates. This in turn requires a reliable method to solve the molecular Schrödinger equation, and in particular, after decoupling of the internal degrees of freedom, an efficient method to solve the vibrational Schrödinger equation. Perturbative methods are not well suited for molecular systems with a high density of states or presenting resonances, and one has to turn oneself towards variational approaches.

One such approach, is the vibrational mean field configuration interaction (VMFCI) method [5–7] implemented in the CONVIV code that has been used in the present work. This flexible method has been shown to converge fundamental frequencies of $\text{C}_2\text{H}_4\text{O}$, an hepta-atomic system [8] presenting strong resonances. Similar accuracy is out-of-reach of the traditional vibrational self-consistent field (VSCF) [9,10]/ vibrational configuration interaction (VCI) (with virtuals from ground state VSCF calculations [11]) approach.

Another necessary condition for obtaining accurate vibrational quantum states, is to employ a good quality vibrational Hamiltonian, that is to say, within the Born-Oppenheimer approximation, a good quality potential energy function, and the relevant rotation-vibration kinetic couplings. We have used in this study on fluoroform the potential energy surface (PES) function of Maynard *et al.* [2], which has been used in many previous works, and can serve as a reference. The PES of Ramesh and Siebert [16] will be used in a forthcoming study.

None of the previous studies on fluoroform using the Maynard *et al.* PES has taken into account the rotation-vibration kinetic couplings. The purpose of the present work is to show to which extent these kinetic couplings in rectilinear coordinates affect the vibrational energy levels.

The letter is organized as follows: First the VMFCI method is briefly outlined and the results obtained without kinetic couplings are compared with other methods for the same PES, in order to assess the convergence of the calculated wave numbers. Then, we show how the kinetic coupling terms of the Eckart-Watson Hamiltonian affect these wave numbers. Finally, we conclude on the importance of adding kinetic couplings terms in the fluoroform vibrational Hamiltonian.

2 CF₃H vibrational states calculation

2.1 The VMFCI method for solving the vibrational Schrödinger equation

Let us briefly sketch out the VMFCI method. The main idea behind it consists in calculating contracted basis sets for groups of degrees of freedom in order to obtain an all-degree basis set of manageable size which captures the physics and can be used for performing a VCI calculation. However, in contrast with the usual contracted VCI approach [12–15] a mean field term is added to the group Hamiltonians and it has been demonstrated that it is the key of the success of the method of contraction [8]. In fact, the VMFCI approach contains the VSCF/VCI method as particular case, but it is much more general, as it allows one to perform successive contracted VCI for arbitrarily selected “active” degrees of freedom in the mean field of the other degrees called “spectator” degrees.

More precisely, at each VMFCI step, one starts with a partition, P , of the n_{vib} vibrational degrees of freedom of an oscillator system into n_P subsets I_1, I_2, \dots, I_{n_P} , of respectively k_1, k_2, \dots, k_{n_P} degrees:

$$\begin{aligned} P &= (I_1, I_2, \dots, I_{n_P}) \\ &= (\{i_1^1, i_2^1, \dots, i_{k_1}^1\}, \{i_1^2, i_2^2, \dots, i_{k_2}^2\}, \dots, \{i_1^{n_P}, i_2^{n_P}, \dots, i_{k_{n_P}}^{n_P}\}), \end{aligned} \quad (1)$$

and defines another partition, S , coarser than or equal to P , that is to say:

$$S = (J_1, J_2, \dots, J_{n_S}), \quad \text{with } n_S \leq n_P,$$

$$\text{and } \forall j \in \{1, \dots, n_P\}, \quad \exists k \in \{1, \dots, n_S\} \quad \text{such that, } I_j \subseteq J_k. \quad (2)$$

The subsets J_k are referred to as “contractions” whose components are the I_j ’s such that $I_j \subseteq J_k$. The number of components in J_k is denoted by l_k .

Assuming that:

(1) The vibrational Hamiltonian can be expanded in a factorized form:

$$\begin{aligned} H_{vib} = h_0 &+ \sum_{j_1=1}^{n_P} h_{j_1}(I_{j_1}) + \sum_{1 \leq j_1 < j_2 \leq n_P} h_{j_1, j_2}(I_{j_1}) h_{j_1, j_2}(I_{j_2}) \\ &+ \dots + h_{1, 2, \dots, n_P}(I_1) h_{1, 2, \dots, n_P}(I_2) \dots h_{1, 2, \dots, n_P}(I_{n_P}) \end{aligned} \quad (3)$$

where $h_{j_1, j_2, \dots, j_k}(I_{j_l})$ denotes a vibrational operator which only depends upon operators acting on the degrees in subset I_{j_l} ,

(2) We have n_P basis sets of vibrational wave functions, $\{\phi_{I_j}^m(q_{i_1^j}, \dots, q_{i_{k_j}^j})\}_{m \in \{1, d_j\}}$, with $1 \leq j \leq n_P$, spanning the Hilbert subspaces of dimension d_j , of physical interest for the groups of degrees of freedom in the I_j ’s,

the VMFCI calculation for that step consists in defining for each contraction, J_k , the mean field Hamiltonian obtained by averaging the vibrational Hamiltonian in the mean field of the other contractions $J_l \neq J_k$ and by diagonalizing it in a basis set of product functions,

$$\Phi_{J_k}^M = \prod_{I_j \subseteq J_k} \phi_{I_j}^{m_j}(q_{i_1^j}, \dots, q_{i_{k_j}^j}), \quad (4)$$

where the superlabel M stands for the sequence of indices m_j of the component functions. That is to say, one first builds a partial Hamiltonian by gathering all the terms of H_{vib} that involve exclusively operators acting on the $I_j \subseteq J_k$,

$$\begin{aligned} H_k = h_0 &+ \sum_{j_1 \text{ such that, } I_{j_1} \subseteq J_k} h_{j_1}(I_{j_1}) \\ &+ \sum_{j_1 < j_2 \text{ such that, } I_{j_1}, I_{j_2} \subseteq J_k} h_{j_1, j_2}(I_{j_1}) h_{j_1, j_2}(I_{j_2}) + \dots \\ &+ \sum_{j_1 < \dots < j_{l_k} \text{ such that, } I_{j_1}, \dots, I_{j_{l_k}} \subseteq J_k} h_{j_1, \dots, j_{l_k}}(I_{j_1}) \dots h_{j_1, \dots, j_{l_k}}(I_{j_{l_k}}), \end{aligned} \quad (5)$$

(where the last sum reduces in fact to only one term). Then, one averages $H_{vib} - H_k$ over a given state, that we have chosen to be, in this work, the product of the ground state functions, $\prod_{I_j \not\subseteq J_k} \phi_{I_j}^0(q_{i_1^j}, \dots, q_{i_{k_j}^j})$, of all the com-

ponents of the spectator contractions. We obtain the mean-field Hamiltonian :

$$H_k + \langle \prod_{I_j \notin J_k} \phi_{I_j}^0(q_{i_1^j}, \dots, q_{i_{k_j}^j}) | H_{vib} - H_k | \prod_{I_j \notin J_k} \phi_{I_j}^0(q_{i_1^j}, \dots, q_{i_{k_j}^j}) \rangle. \quad (6)$$

This Hamiltonian is diagonalized in the basis set of all product functions of Eq.(4), or in a subset of the latter obtained by selecting the product functions such that the sum of the energies of their components is below a given threshold. Additionally, extra threshold can be applied to the energy of any component.

2.2 CF_3H rectilinear coordinate vibrational Hamiltonians

Fluoroform belongs to the C_{3v} symmetry point group. It has nine vibrational degrees of freedom and six normal modes. According to spectroscopic labelling, ν_1 to ν_3 (A_1 symmetry) correspond to CH stretching (Q_1), CF_3 symmetric stretching (Q_2) and CF_3 symmetric deformation (Q_3) respectively, and ν_4 to ν_6 (E symmetry) correspond to FCH bending (Q_{4a}, Q_{4b}), CF_3 asymmetric stretching (Q_{5a}, Q_{5b}) and CF_3 asymmetric deformation (Q_{6a}, Q_{6b}) respectively.

The Hamiltonians used in this study can be expressed as

$$H_{vib} = \sum_{k=1}^{6b} P_k^2 + P_1 \cdot (\alpha P_2 + \beta P_3) + V(Q_1, \dots, Q_{6b}) + W(Q_1, P_1, \dots, Q_{6b}, P_{6b}). \quad (7)$$

In this expression, V is the Born-Oppenheimer PES term. The PES used in this study has been calculated by Maynard *et al.* [2]. It is expressed in rectilinear coordinates, and uses a local coordinate description of the CH stretching and a normal coordinate description for the other modes. The 3D chromophore (Q_1, Q_{4a}, Q_{4b}) is described by a 14th-order Taylor expansion while a fourth-order expansion is used for the other modes and intermode couplings. The resulting Born-Oppenheimer potential operator contains 467 terms, that have the form of a product of powers of the coordinates. In addition, the pure, local mode dimension is described by a Morse potential term. So, the potential is expanded as a sum of product terms as in equation (3), and is amenable to effective VMFCI calculations. This PES has been computed at the (6-311G**/MP2) level of theory and the chromophore part was improved by using a more accurate method (cc-PVTZ/CEPA-1). The PES has been estimated [4] to be sufficiently accurate up to 9500 cm^{-1} excitation energy in the bath modes and up to 15000 cm^{-1} for the chromophore.

In eq.(7), the P_k are the conjugate momenta of the Q_k . Because, the local mode Q_1 is close to, but not exactly equal to the corresponding normal mode, a first order corrective term, coupling P_1 to the two other A_1 -modes conjugate momenta appears in the Maynard *et al.* Hamiltonian [2].

The last term in eq.(7) is the ($J = 0$)-Watson-Eckart Hamiltonian rotation-vibration kinetic coupling term,

$$W(Q_1, P_1, \dots, Q_{6b}, P_{6b}) = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \pi_\alpha \pi_\beta - \frac{1}{8} \sum_{\alpha} \mu_{\alpha\alpha}, \quad (8)$$

where π is the so-called “Coriolis coupling operator” and μ is the 3×3 matrix derived from the inertia tensor. Rigorously speaking, the coordinates and conjugate momenta appearing in the latter two operators should be the rectilinear normal ones. However, since W is only a corrective term and since the projection of the local mode coordinate on the normal CH-stretch coordinate is close to one (α and β small in eq.(7)), the difference between the local and the normal CH-mode has been neglected in W . This zeroth-order approximation is indeed consistent with the use of a first order approximation in the second term of eq.(7).

In practice, the W term used in this study has been obtained by expanding the μ -matrix in power of the Q_k ,

$$\mu = \sum_{n=0}^{+\infty} \left(\frac{1}{2}\right)^n (n+1) \times \sum_{k_1, \dots, k_n} I_e^{-1} a_{k_1} I_e^{-1} \dots a_{k_n} I_e^{-1} Q_{k_1} \dots Q_{k_n} \quad (9)$$

where I_e^{-1} is the inverse of the inertia tensor $I(Q_1, \dots, Q_{6b})$ at equilibrium and $(a_k)_k$ are the derivatives of the latter with respect to the normal coordinates at the equilibrium geometry (assuming that it is also the Eckart frame reference geometry, as is common practice),

$$a_k = \left(\frac{\partial I}{\partial Q_k}\right)_0. \quad (10)$$

Previous studies using the Maynard *et al.* Hamiltonian have neglected W . This correspond to setting $\mu = 0$. We call “order X” those calculations that use this ($\mu = 0$)-Hamiltonian. Other calculations performed in this work have been obtained by truncating the expansion (9) at a given order, say n , and are called “order n ” calculations.

2.3 Selection of the VMFCI contraction scheme

The VMFCI contraction scheme selected in this study starts as usual [7] with minimal symmetry preserving (MSP) steps which consist in contracting the degenerate modes together and only them, and which, as the name indicates, prevent artefactual symmetry breaking to occur. This is in contrast with the VSCF method which usually lift artefactually the degeneracy [17]. For fluoroform, MSP-VMFCI wavefunctions have the product form,

$$\phi_1(Q_1)\phi_2(Q_2)\phi_3(Q_3)\phi_4(Q_{4a}, Q_{4b})\phi_5(Q_{5a}, Q_{5b})\phi_6(Q_{6a}, Q_{6b}). \quad (11)$$

The MSP partition has been iterated 6 times until self-consistency was achieved to machine (double) precision, which means that a MSP vibrational self-consistent field configuration interaction calculation (MSP-VSCFCI) has been performed.

Next, for selecting the contraction scheme of the MSP-VSCFCI basis set, we have calculated the ZPE value for all different two-mode contractions. They are reported in Table 1, the contractions being ordered by increasing ZPE values. Clearly, the most efficient contraction in terms of ZPE lowering is the $\{\nu_1-\nu_2\}$ contraction, whose ZPE lowering (19 cm^{-1}) is an order of magnitude larger than the next one in the list (2 cm^{-1}), in spite of the fact that only two degrees of freedom are involved, whereas other contractions can involve up to three or four degrees. So, on this ground, we have decided to contract modes $\{\nu_1-\nu_2\}$ straight after the MSP-VSCFCI.

Since in this study, we focus on the $\{\nu_1-\nu_4\}$ chromophore and since resonances between modes ν_1 and ν_4 excited states do not necessarily show up with the ZPE lowering criterium, we have actually opted for the ternary contraction $\{\nu_1-\nu_2-\nu_4\}$ which lowers the ZPE by 22 cm^{-1} . We have not considered larger contraction than this 4-degrees contraction, because it would have been less computer effective given the limited RAM space of our computer: The integral file loaded in RAM at the next VMFCI step would require too drastic an energy truncation threshold to fit in.

Iterating the VMFCI($\nu_1-\nu_2-\nu_4$) step once has been found to be sufficient to achieve self-consistency. Finally, the VSCFCI($\nu_1-\nu_2-\nu_4$) has been followed by several all-degree VCIs differing from their truncation thresholds in the last step.

2.4 Convergence of the VMFCI calculations

Table 2 reports the results obtained with the VMFCI contraction scheme described above for different truncation schemes at the last step. These calculations have been performed with the Hamiltonian, Eq. (7), and no rotation-vibration kinetic coupling ($W = 0$). We have neglected the Eckart-Watson term, Eq. (8), to be able to compare our results with those obtained in other studies [2–4] where the same Hamiltonian was used.

The first column of Tab. 2 provides the assignment of the vibrational states in terms of harmonic functions or Morse potential eigenstates of highest weight as reported in previous studies [3,4]. However, these basis functions are highly mixed due to the presence of resonances as seen from the expansion of excited states such as $4\nu_4$, $\nu_1 + 2\nu_4$ and $2\nu_2$ (see Tab.V of [3] and Tab. 3). In our VSCFCI(ν_1 - ν_2 - ν_4) and VCI calculations, it is more natural to assign states in terms of the MSP-VSCFCI basis functions. Using the MSP-VSCFCI functions of highest weight, we find the same labelling for the vibrational states than that of Tab. 2 except for the excited states $4\nu_4$ and $\nu_1 + 2\nu_4$ which are inverted, moreover the $\nu_1 + 2\nu_4$ VSCFCI(ν_1 - ν_2 - ν_4)-eigenfunction has in fact its highest weight on the $2\nu_1$ MSP-VSCFCI basis function (see Tab. 3).

The second column of Table 2 reports the harmonic approximation frequencies (modes ν_2 to ν_6) and for mode ν_1 the Morse potential approximation. All VMFCI calculations start with a MSP-VSCFCI calculation using a basis set of harmonic oscillator (HO) functions with quantum numbers less than 60,40,40,40,40,60, respectively, for the vibrational modes $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$, respectively. (Integrals of the Morse potential function between HO wave functions are calculated analytically in our code CONVIV by using the formulas of Ref. [18].) The results are reported in the third column and show large deviations with respect to the Harmonic/Morse approximation due to the anharmonicity of the system.

The next column correspond to the subsequent VSCFCI(ν_1 - ν_2 - ν_4) with truncation of the product basis set on the sum of the energies at 24000 cm^{-1} . In this calculation, the basis sets of the other modes have also been truncated at 24000 cm^{-1} for practical purposes, but this has no influence on the end results. We observe again large deviations for the contracted modes with respect to the MSP-VSCFCI results. In particular, the chromophore overtones change by more than 100 cm^{-1} for the $2\nu_1$ and by as much as 300 cm^{-1} for the $4\nu_4$. This fully justifies *a posteriori* the inclusion of mode ν_4 in the contraction.

The VCI results (fifth column) have been obtained with a truncation on the sum of the energies at 10200 cm^{-1} and a truncation on the energy of mode ν_6 at 6000 cm^{-1} . The total number of basis functions is 67092 and the VMFCI

scheme reads in rather self-explanatory notation (defined explicitly in ref. [7]), MSP-VSCFCI(60,40,40,40,40,60)/VSCFCI(ν_1 - ν_2 - ν_4 ;24000)/VCI(*,*,*,6000|10200) (No truncation on a given contraction component is indicated by a “*” symbol.)

These results are to be compared with those reported in the last column obtained with the multi-configuration time dependent Hartree-Fock (MCTDH) approach ([4] and [19] for wave numbers below 3049 cm^{-1}), which is also a variational method. These MCTDH wave numbers are very close to the wave operator sorting algorithm (WASO) wave numbers [3] not reported here. We see that the VCI and MCTDH ZPE are the same to the hundredth of cm^{-1} and that all tabulated VCI wave numbers are within 1 cm^{-1} of the MCTDH ones. In the bottom part of the spectrum, they are within the tenth of cm^{-1} of the MCTDH ones. This good agreement allows us to be confident in the reliability of our VMFCI scheme for the assessment of the rectilinear coordinates, rotation-vibration kinetic couplings which have not been considered in previous variational studies so far. The evaluation of these couplings will be the topics of the next section.

The effect of the VCI truncation thresholds on the tabulated wave numbers are investigated in Table 4. The two middle columns correspond to the same threshold of 10000 cm^{-1} on the sum of the components function energies in product basis functions. In addition, a threshold of 6000 cm^{-1} is applied on the ν_6 -component function energy in the calculation presented in the second column. This reduces the basis set size by 2312 basis function. However, the tabulated wave numbers are identical in the two columns except for $4\nu_4$ where they differ by 0.1 cm^{-1} . So, including excited ν_6 MSP-VSCFCI basis function is not crucial for the eigenstates of interest and the use of a threshold on the ν_6 -component function energy is justified in Tab.2.

Columns 1, 2 and 4 of Tab. 4 shows the convergence pattern with respect to the threshold on the sum of the component energies. The bottom of the spectrum is already well converged with a threshold of 9800 cm^{-1} and less than 53000 basis functions. Only the three levels of the chromophore $2\nu_1$ -polyad are not yet converged. The threshold at 10000 cm^{-1} adds 6722 basis functions and improves the polyad wave numbers significantly if the calculation with the 10200 cm^{-1} threshold serves as a reference. On the basis of the wave number convergence pattern, one can reasonably expect to have reached the cm^{-1} accuracy with the latter calculation.

3 Effect of the rectilinear coordinate rotation-vibration kinetic coupling

Vibrational levels computed at different orders of μ -matrix expansion are reported in Table 5. Order X corresponds to column 3 of Tab. 4. The results for the other orders of μ -matrix expansion have been obtained with the same contraction-truncation scheme. It is clear that the ($W = 0$)-Hamiltonian is not satisfactory because some fundamental frequencies are away from those of order 1 by more than the 1 cm^{-1} . The largest errors are observed for the ν_2 fundamental wave number ($\approx 16 \text{ cm}^{-1}$) and for ν_1 ($\approx 37 \text{ cm}^{-1}$). For higher excited states, the discrepancies grow even larger: $\approx 56 \text{ cm}^{-1}$ for $4\nu_4$, $\approx 62 \text{ cm}^{-1}$ for $\nu_1 + 2\nu_4$, and $\approx 58 \text{ cm}^{-1}$ for $2\nu_1$.

In contrast, the results show that Order 0 is sufficient to take into account the kinetic coupling effect. The difference between Order 0 and Order 1 is equal to less than the tenth of cm^{-1} for all vibrational levels, (the errors of 0.1 cm^{-1} appearing in the table are due to round off of the last digits).

The inclusion of the kinetic coupling can bring some vibrational frequencies closer to the experimental ones [20] like for mode ν_2 but this is not general. This hints to the fact that a better description of the PES is required to improve the agreement with the experimental data.

4 Conclusion

In this study, we have performed large variational calculations of the vibrational eigenstates of fluoroform by using an efficient vibrational Schrödinger equation solver, the VMFCI method. The accuracy of the eigenstates obtained have been checked against MCTDH results. Then, we have investigated the importance of the rotation-vibration kinetic coupling in rectilinear coordinates on the spectrum calculation. We have shown that it is not negligible, however a zero order expansion of the μ -matrix is sufficient to account for the coupling.

A natural follow-up to the present work will be the evaluation of the influence of the rotation-vibration kinetic coupling terms on intramolecular vibrational energy redistribution in highly excited fluoroform.

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References

- [1] O. Boyarkin, M. Kowalszyk and T. Rizzo, J. Chem. Phys 118 (2003) 93.
- [2] A. T. Maynard, R. E. Wyatt and C. Iung, J. Chem. Phys. 103 (1995) 8372
- [3] A. T. Maynard, R. E. Wyatt and C. Iung, J. Chem. Phys. 106 (1997) 9483
- [4] C. Iung and F. Gatti, H. D. Meyer, J. Chem. Phys. 120 (2004) 6992
- [5] P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. 93 (2003) 245-264.
- [6] P. Cassam-Chenaï, J. Quant. Spectrosc. Radiat. Transfer 82 (2003) 251-277.
- [7] P. Cassam-Chenaï, J. Liévin, Journal of Comp. Chem. 27 (2006) 627-640.
- [8] D. Bégué, C. Pouchan, N. Gohaud, P. Cassam-Chenaï, J. Liévin, J. Chem. Phys 127 (2007) 164115-164124.
- [9] J. M. Bowman, J. Chem. Phys 68 (1978) 608.
- [10] G. D. Carney, L. L. Sprandel and C. W. Kern in “Advances in Chemical Physics”, Vol. 37, I. Prigogine and S.A. Rice, Eds., (Wiley, New York, 1978), pp. 305-379.
- [11] K. M. Christoffel, J. M. Bowman, Chem. Phys. Lett. 85 (1982) 220.
- [12] C. L. Chen, B. Maessen, and M. Wolfsberg, J. Chem. Phys 83 (1985) 1795.
- [13] J. Tennyson, Comp. Phys. Rep. 4 (1986) 1.
- [14] S. Carter and N. C. Handy, Comp. Phys. Rep. 5 (1986) 15.
- [15] Z. Bačić and J. C. Light, Annu. Rev. Phys. Chem. 40 (1989) 469.
- [16] S. G. Ramesh and E. L. Sibert, Mol. Phys. 103 (2005) 149.
- [17] R. Burcl, S. Carter, N. C. Handy, Chem. Phys. Lett. 373 (2003) 357-365.
- [18] P. Palting, S. T. Lai, Y. N. Chiu, J. R. Letelier, J. Math. Chem. 21 (1997) 31.
- [19] F. Gatti, private communication
- [20] H. R. Dübal and M. Quack, J. Chem. Phys. 81 (1984) 3779

$\nu_1-\nu_2$	$\nu_1-\nu_4$	$\nu_1-\nu_3$	$\nu_1-\nu_6$	$\nu_4-\nu_5$	$\nu_4-\nu_6$	$\nu_2-\nu_4$	$\nu_2-\nu_3$
5648.68	5665.31	5665.70	5665.92	5666.77	5667.13	5667.23	5667.38
$\nu_3-\nu_5$	$\nu_3-\nu_6$	$\nu_5-\nu_6$	$\nu_3-\nu_4$	$\nu_1-\nu_5$	$\nu_2-\nu_6$	$\nu_2-\nu_5$	
5667.44	5667.48	5667.57	5667.59	5667.60	5667.60	5667.60	

Table 1

Zero point energy in cm^{-1} after a MSP-VSCFCI(60,40,40,40,40,60) calculation followed by two-mode contractions. The ZPE are arranged in increasing order. For comparison, the MSP-VSCFCI ZPE is 5667.61 cm^{-1} . The product basis functions for the two-mode contractions have been truncated at 11400 cm^{-1} on the sum of the component energies.

assign.	Morse/HO	MSP-VSCFCI	VSCFCI($\nu_1 - \nu_2 - \nu_4$)	VCI	MCTDH ^a
ZPE	5701.83	5667.61	5645.61	5638.54	5638.54
ν_6	518.2	509.4	509.4	507.0	507.0
ν_3	724.3	712.9	712.9	703.7	703.7
ν_2	1203.6	1200.9	1167.9	1157.8	1157.8
ν_5	1206.0	1190.3	1190.0	1175.8	1175.8
ν_4	1431.0	1416.6	1407.4	1396.2	1396.2
$2\nu_4$	2861.9	2862.6	2777.2	2750.0	2749.7
ν_1	3069.6	3014.0	3057.4	3048.9	3048.7
$4\nu_4$	5723.9	5789.3	5489.9	5435.1	5436
$\nu_1 + 2\nu_4$	5931.5	5876.6	5804.6	5758.0	5759
$2\nu_1$	6013.8	5899.3	6009.3	5988.2	5989

Table 2

Energies in cm^{-1} of the vibrational fundamental transitions and of the overtones of the $(\nu_1 - \nu_4)$ -chromophore calculated at different VMFCI levels (see text for details) and with the MCTDH algorithm. The tabulated energies of the $2\nu_4, \nu_1 + 2\nu_4, 4\nu_4$ bands are those of their non degenerate levels.

^a Ref. [4], and [19] for wave numbers below 3049 cm^{-1}

	VSCFCI($\nu_1 - \nu_2 - \nu_4$)	$ \Phi_{4\nu_4}^{\text{MSP}}\rangle$	$ \Phi_{\nu_1+2\nu_4}^{\text{MSP}}\rangle$	$ \Phi_{2\nu_1}^{\text{MSP}}\rangle$
$4\nu_4$	5489.9	0.39	0.46	0.06
$\nu_1 + 2\nu_4$	5804.6	0.38	0.10	0.46
$2\nu_1$	6009.3	0.15	0.37	0.42

Table 3

Projection weights of contracted VSCFCI($\nu_1 - \nu_2 - \nu_4$) eigenfunctions of Tab. 2 on relevant MSP basis functions.

assign.	VMFCI(9800)	VMFCI(10000)	VMFCI ^(*) (10000)	VMFCI(10200)
	52964 bf.	59686 bf.	61998 bf.	67092 bf.
ZPE	5638.54	5638.54	5638.54	5638.54
ν_6	507.0	507.0	507.0	507.0
ν_3	703.7	703.7	703.7	703.7
ν_2	1157.8	1157.8	1157.8	1157.8
ν_5	1175.8	1175.8	1175.8	1175.8
ν_4	1396.3	1396.3	1396.3	1396.2
$2\nu_4$	2750.1	2750.0	2750.0	2750.0
ν_1	3049.0	3048.9	3048.9	3048.9
$4\nu_4$	5439.8	5436.4	5436.3	5435.1
$\nu_1 + 2\nu_4$	5761.5	5759.7	5759.7	5758.0
$2\nu_1$	5989.5	5990.2	5990.2	5988.2

Table 4

Convergence of vibrational levels with different VCI basis set truncation scheme. VMFCI actually stands for the contraction scheme: MSP-VSCFCI(60,40,40,40,40,60)/VSCFCI(ν_1 - ν_2 - ν_4 ;24000)/VCI, and the value in parenthesis is the threshold in cm^{-1} applied to the sum of the energies of the product function components for the VCI. For all calculations, a truncation at 6000 cm^{-1} was applied to the energy of mode ν_6 component except for VMFCI^(*)(10000). “bf.” stands for basis functions.

assign.	Ord X	Ord 0	Ord 1	Expt ^b
ZPE	5638.54	5652.28	5652.28	-
ν_6	507.0	507.1	507.1	507.8
ν_3	703.7	703.6	703.6	700.1
ν_2	1157.8	1141.6	1141.7	1141.5
ν_5	1175.8	1176.5	1176.5	1158.3
ν_4	1396.3	1398.4	1398.5	1377.5
$2\nu_4$	2750.0	2768.2	2768.2	2710.2
ν_1	3048.9	3086.1	3086.1	3035.5
$4\nu_4$	5436.3	5492.0	5492.1	5337
$\nu_1 + 2\nu_4$	5759.7	5821.5	5821.6	5710.4
$2\nu_1$	5990.2	6048.3	6048.4	5959.4

Table 5

Energies in cm^{-1} of fluoroform vibrational states calculated at different order of μ -matrix expansion (Order X corresponds to setting $\mu = 0$). The tabulated values are obtained from a VCI at the last step with a truncation on the sum of the energies of product function components at 10000 cm^{-1} and are expected to be converged to the cm^{-1} precision.

^b Ref. [20]